Pesticide contamination in ambient air in Germany. Results with focus on the northern glacial lake district.

A Germany-wide study to determine the occurrence of pesticides in ambient air, honeybee bread, filters from ventilation systems and air quality bark monitoring were analysed for the presence of over 500 pesticides and their related active substances including glyphosate.

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Abstract

For the Federal Republic of Germany, the present study is the most comprehensive collection of data on the occurrence and distribution of pesticides in the air. Within a year of measuring the results show that the existence of uncontaminated sites is very unlikely which rises the question of effects on protected areas, for example in the northern glacial lake district.

The number and composition of the pesticides found as well as the level of exposure depend on the sampling site, the sampling media and on the characteristics of the pesticides. The contamination tends to be higher in Northern Germany where an intensive use of pesticides can be assumed. The distance to the next potential source however had little impact. Even in nature reserves as large as the "Bayerischer Wald" a cocktail of pesticides is found in the air.

The results gathered through non-biological collection media indicate that glyphosate is wider spread in the air than any of the other active substances. It is the first time that the omnipresence of glyphosate in ambient air has been documented to this extent.
The long-term risks posed to humans and ecosystems by continuous exposure to mixtures of enzymatically active substances in ambient air are still unknown.

Tree bark measurements were already taken between 2014 and 2018 in the biosphere reserve of Schorfheide-Chorin, an area with mainly organic farming, and provided a first indication that pesticides used in conventional agriculture can be widely distributed through the air (Hofmann, Schlechtriemen et al. 2019). The purpose of the following study (Kruse-Plaß et al. 2020) was to expand these results by using a number of additional methods to measure the pesticide contamination in the air.

For this purpose, in 2019, 116 sites across the Federal Republic of Germany were examined as part of a Citizen Science project. The following collection methods were employed: technical passive samplers (49 samples), filter mats from ventilation systems (20 samples), honeybee bread (41 samples) and additional tree bark samples (6 samples). The samples were analysed by using multi-analysis for over 500 pesticide active substances including glyphosate and its metabolite AMPA and glufosinate. The results were compiled with data from earlier bark analyses from the years 2014 to 2018 (47 samples).

- In 163 samples, a total of 152 active substances were detected
- 138 were attributable to agricultural sources.
- Out of these, 41 active substances (30 percent) are no longer licensed for use in the Federal Republic of Germany.

Results of different collection methods

In general, passive samplers provided the most meaningful results. A total of 80 active substances were detected. The analytical results are based on the government guideline for the detection of pesticide residues in food stuff (ASU L 00.00 – 115, compiled by the BVL (Bundesamt für Verbraucherschutz und Lebensmittelsicherheit; BVL 2018).

In a second step the detected active substances were reduced to contain only agents with an agricultural origin. After excluding PCB (5) and other substances of non-agricultural origin (4) from the original list, 71 active substances remained of which 5 to 31 were detected per sampling site. In the passive samplers, the median of the number of active substances is 17.

The active substances most commonly found were glyphosate, chlorothalonil, metolachlor, pendimethalin, terbuthylazine, prothioconazole-desthio, dimethenamide, prosulfocarb, AMPA, flufenacet, tebuconazole, aclonifene, chlorflurenol, HCH-gamma (lindane), MCPA, epoxiconazole and folpet. The active substances listed were detected at least at one third of the 49 passive sampling sites. Glyphosate was the only substance detected in all samples of non-biological origin (100 percent of all sites with passive samplers and filter mats).

While the PUF matrix in passive samplers absorbs volatile pesticide active substances, filter mats in ventilation systems are designed to filter dust particles from the air. It can therefore be assumed that the pesticides detected in filter mats initially adhered to soil particles which, transported by wind, were caught in the filter of the ventilation system. In the 20 samples 62 pesticide active substances with a primarily agricultural origin were detected. Sites were contaminated with between one and 34 active substances.

For honeybee bread the collection spectrum is different again. Unlike passive samplers and filter mats, honeybee bread reflects the bees' exposure to insecticides such as thiacloprid. In 41 samples, 48 pesticide active substances were found, with 0 to 12 active substances per site.

The samples from tree bark monitoring show the widest range of pesticide active substances. In 53 samples 94 active substances were found in total and at each site 1 to 26 pesticides were present. - Fig.1 shows the regional distribution of sampling sites in northern Germany and numbers of active substances detected in different media as barplots. Table 1 supplements numerical information.

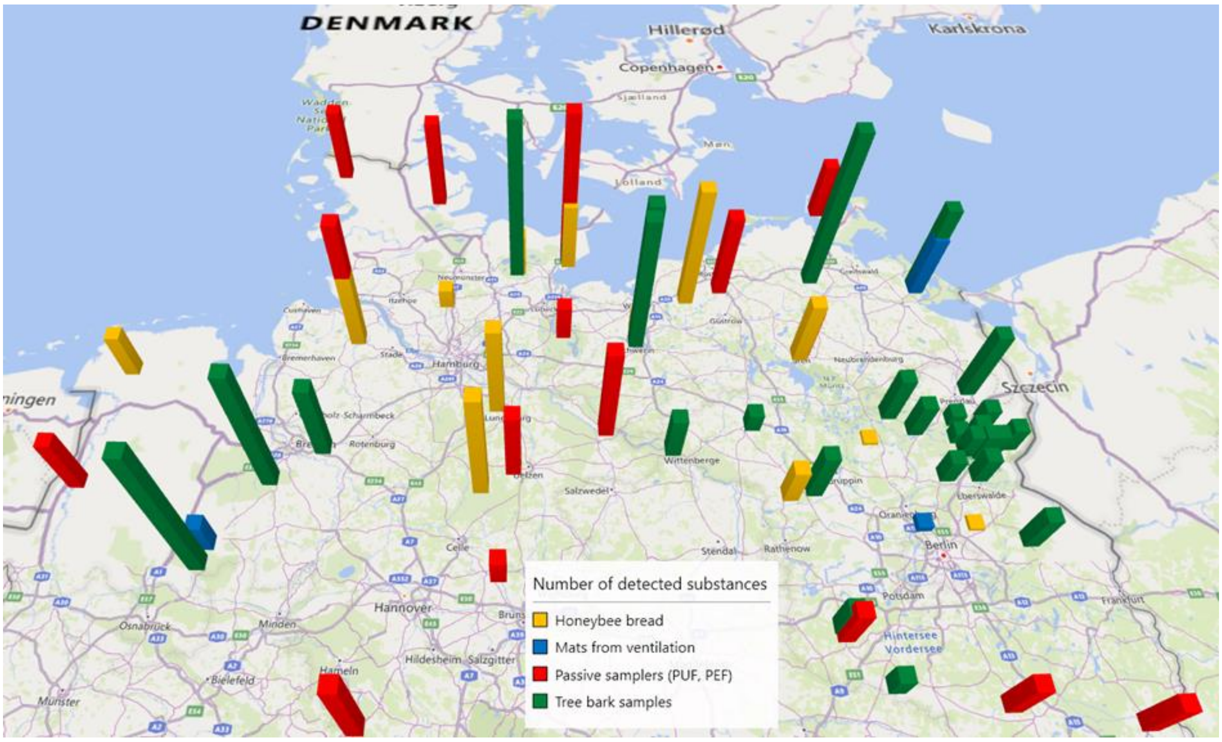

Fig. 1: Detected substances at sampling sites in northern Germany
(adapted from Kruse-Plaß et al. 2020). The height of each bar is scaled to the number of detected substances (cf. Table 1). Data for passive samplers and mats from ventilation systems were collected after exposure between mid-march to mid november 2019. Honeybee bread samples were collected within this period, tree bark samples between 2014 to 2018.

Examinded Media	Number of samples	Number of detected substances
Passive samplers	14	14 - 27
Honeybee bread	13	1 - 12
Mats from ventilation systems	4	2 - 10
Tree bark samples (2014 - 2018)	30	1 - 25

Table 1: Per sampling site detected substances in Schleswig-Holstein, Niedersachsen, Mecklenburg-Vorpommern and Brandenburg

Statistical analysis

The statistical analysis examines six locational factors for their effect on the measured values. It identifies the natural area of the site and the intensity of agriculture as important influencing factors in the passive samplers. The distance to the nearest potential source and the location in a nature reserve has little impact on the values detected. Also, the orientation of a site towards organic management, wind erosion classification of the underlying soil and the biogeographical area have no effect on the number of observed active substances. Only for metolachlor significantly lower values can be found in areas with a high percentage of organic farming. The data are complexly linked and must be considered separately for each active substance investigated. The composition of the active substances detected varies for the different media tested.

Active substances at selected sites in the northern glacial lake district

The glacial northern lake district extends from Eastern Schleswig-Holstein to Mecklenburg-Vorpommern and North Brandenburg up to and over the Polish border. Apart from the biosphere reserve Schorfheide-Chorin in north-eastern Brandenburg the district is rich in natural reserves with unique lakes and large forest areas.

Table 2: Organic contaminants with agricultural origin detected in passive samplers at 2 sites in Ostholstein resp. Waren/Mecklenburg-Vorpommern (site Nr.808 resp. Nr.707) in comparison to summarized data from tree bark monitoring.

cf. tab.18 in Kruse-Plass et al. 2020 and tab.32 /»PAS Ergebnisse 2019.xlsx«
https://www.enkeltauglich.bio/wp-content/uploads/2020/09/PAS-Ergebnisse-2019.xls

targets: **H** herbicide **F** fungicide **I** insecticide **-M** metabolite
HRAC mode of action classification for herbicides:
F4, S carotenoid synthesis/ bleaching **O** auxine
G EPSP-synthase **H1** Glutam.-Ammon.-Ligase /photosynthesis
K1 Microtubuli /cell division **K3** fatty acid synthesis /cell division

target	HRAC	active substance	passive sampler number 808 (ng/sample)	passive sampler number 707 (ng/sample)	tree bark monitoring total amount (ng in 53 samples)
H	G	glyphosate	77	158	498
H-M		AMPA	31	45	
H	S	aclonifen	17	26	
F		boscalid			318
H		chlorflurenol		108	
I		chlorpyrifos-et	18		
F		chlorthalonil	273	1090	
H	F4	clomazone	26	209	
I		DDT & metabolites		14	1619
H	K3	dimethenamid	60	15	
F		epoxiconazoe	17		
H	K3	flufenacet	22		
F		fluopyram	13	61	
F		folpet	11		
I		HCH gamma /lindane	33		252
H	O	MCPA	11	10	
H	K3	metazaclor		105	
H	K3	metolachlor	149	60	656
H	K1	pendimethalin	1249	1812	1384
H	K3	prosulfucarb	494	26	441
F-M		prothioconazole-desthio	81	201	881
F		tebuconazole	14	53	
H	H1	terbuthylazine	62	77	781

Substances analysed at the passive sampler sites Nr. 808 in eastern Schleswig-Holstein and Nr.707 in Mecklenburg/ Waren and in tree barks are listed in table 2 with amounts and targets, for herbicides with HRAC codes for mode of action. 12 herbicides, 6 fungicides, 3 insecticides and 2 metabolites were detected at these sites. Insectides of the DDT-group and Lindan found in higher amounts in tree barks can be traced back to excessiv application in the former DDR. Half of the herbicides found are classified as inhibiting cell division and are broadly used in post-emergence treatment to suppress seedlings concurring with cultured plants. A special case and cause for concern is terbuthylazine that blocks photosynthesis and is widely found in air according to its application in corn fields and relative persistence together with its relevant metabolite desethl-TBA. Glyphosate is a special case too as it currently is the most frequently applied and sold pesticide in spite of longterm detrimental effects below regulatory accepted effect tresholds. In plants and microorganismens it blocks the Shikimat metabolism. Adverse effects at sublethal concentrations have been found in vertebrates, e.g. cellular and enzymatic damages in fishes.

Discussion

Our finding of a widespread airborne contamination in Germany is confirmed by results from Sweden and rises concerns regarding possible impacts on human health and environment.

The Swedish monitoring programme on the environmental fate of pesticides includes air measurements since 2009 (Kreuger and Lindström 2019). 33 pesticides were detected in more than 20% of rain water samples and 15 thereof were not approved in Sweden. The data show long distance transport of substances such as triallate, terbuthylazine, flufenacet, metolachlor and chlorpyrifos for example. Tracking back movements of air masses associated with rainfall events carrying such substances, the authors found their origin in middle Europe. For a central European country such as Germany correspondingly is to expect a considerable amount of long-range as well as transboundary transport. An example in our data is chlorpyrifos, which is not approved in Germany either. Furthermore, our statistical analysis could not identify the distance to a potential source as a major influence on the measured values at the investigation site. This result, together with the number of substances detected in nature and biosphere reserves and national parks, is a strong indication for airborne contamination of sensitive environments by supraregional transport of pesticides and their metabolites.

Clausing (2020) discussed potential effects to human health of pesticides detected in tree bark by Hofmann et al. (2019). He outlined deficits in current risk assessments and missed data regarding effects of exposure to pesticide mixtures. In ecotoxicological risk assessment,"the gap between intention and reality" (Schäfer et al. 2019) is even larger than in human risk assessment. The complexity of ecosystems simply renders effects of anthropgenic stressors unpredictable. And the cocktail of airborne pesticides detected targets vital functional groups and functions of ecosystems.

The adsorption on the surface of passive samplers can be compared to the uptake of toxic substances via biological surfaces, especially those controlling the exchange of organisms with their surroundings, and can be considered as a first information about otherwise yet unknown airborne toxic stress on lungs, gills, guts, leaves, roots, mycorrhizza, cell walls and microbioms.

Remains the question whether the degree of airborne organic contamination is ecotoxicologically relevant or not. Comparing concentrations of pesticides measured in rain water with known ranges of ecotoxicogical effects concentrations may lead to a tentative answer.

Concentrations of pesticides in rainwater have been regularly reported in the past exceeding 0,1 µg/l with maxima in the range of several µg/l (Dubus et al. 2000, Stähler 1993). York and Kreuger (2019) accordingly found concentrations in rainwater not seldom exceeding 0,1 µg/l, values for terbuthylazine (non-registered in Sweden) often in the range of 1 µg/l and a maximum value of 3,8 µg/l for prosulfocarb.

0,1 µg/l of an active ingredient (a.i.) of a pesticide is the threshold value set as safe for human health by drinking water regulations in European countries, with 1 µg/l for the sum of detected a.i.s in one sample. With respect to this general limit, a.i.s in rainwater should be too much diluted in deep lake waters to cause effects. Effects in shallow waters however cannot be excluded nor can effects on biota above and below-ground be excluded, particularly combined effects of the sum of airborne volatile, particle-bound and soluted a.i.

Along this line it cannot be excluded either that e.g. species losses monitored over the last decades in protected areas, otherwise out of range of agricultural inputs, might be related to a certain extent to airborne toxic inputs. If one accepts that pesticides in air might affect biota, one has to face the possibility that they might impair the resilience of communities and contribute to shifts, especially in combination with other anthropogenic stressors e.g. in course of climate change.

Remains an urgent need to investigate the possible ecotoxicological relevance of airborne contamination by toxic organic substances with agricultural origin.

References

BVL, Bundesamt für Verbraucherschutz und Lebensmittelsicherheit (2019a). Widerruf der Zulassung von Pflanzenschutzmitteln mit dem Wirkstoff Chlorothalonil zum 31. Oktober 2019. Vom 19.06.2019. "Fachmeldungen aus dem Arbeitsbereich "Pflanzenschutzmittel". Retrieved 21.04.2020, from https://www.bvl.bund.de/SharedDocs/Fachmeldungen/04_pflanzenschutzmittel/2019/2019_06_19_Fa_Widerruf_Chlorothalonil.html

BVL, Bundesamt für Verbraucherschutz und Lebensmittelsicherheit (2019b). Vom 21.06.2019. "Fachmeldungen aus dem Arbeitsbereich "Pflanzenschutzmittel". Retrieved 21.04.2020, from https://www.bvl.bund.de/SharedDocs/Fachmeldungen/04_pflanzenschutzmittel/2019/2019_06_21_Fa_Nichtgenehmigung_Chlorpropham.html

BVL, Bundesamt für Verbraucherschutz und Lebensmittelsicherheit (2018): Untersuchung von Lebensmitteln - Multiverfahren zur Bestimmung von Pestizidrückständen mit GC-MS und LCMS/MS nach Acetonitril-Extraktion/Verteilung und Reinigung mit dispersiver SPE in pflanzlichen Lebensmitteln - Modulares QuEChERS-Verfahren. (Neufassung der Methode L 00.00-115 durch die Arbeitsgruppe „Pestizide" nach § 64 LFGB). Beuth Verlag.

Clausing, P. (2020). Baumrinden-Monitoring der Pestizid-Belastung über die Luft: Eine oekotoxikologische Bewertung. Retrieved 20.04.2020 from https://www.enkeltauglich.bio/?page_id=721.

Dubus I.G., Hollis J.M., Brown, C.D. (2000): Pesticides in rainfall in Europe. –Environmental Pollution 110, p. 331-344

Hofmann, F., U. Schlechtriemen, M. Kruse-Plaß and W. Wosniok (2019). Biomonitoring der Pestizid-Belastung der Luft mittels Luftgüte-Rindenmonitoring und Multi-Analytik auf >500 PSM-Wirkstoffe sowie Glyphosat. Dortmund: TIEM Integrierte Umweltüberwachung. http://enkeltauglich.bio/wp-content/uploads/2019/02/Bericht-H18-Rinde-20190210-1518-1.pdf

Kreuger, J. und Lindström, B. (2019). Long-term monitoring of pesticides in air and atmospheric deposition in Sweden. IUPAC. Ghent, Belgium 20 May 2019.

Kruse-Plaß, M., W. Wosniok und U. Schlechtriemen (2020). Pestizid-Belastung der Luft. Eine deutschlandweite Studie zur Ermittlung der Belastung der Luft mit Hilfe von technischen Sammlern, Bienenbrot, Filtern aus Be- und Entlüftungsanlagen und Luftgüte-Rindenmonitoring hinsichtlich des Vorkommens von Pestizid-Wirkstoffen, insbesondere Glyphosat. https://www.ackergifte-nein-danke.de/wp-content/uploads/2020/09/Studie_final_niedrig.pdf

Schäfer, R. B., Liess, M., Altenburger, R., Filser, J., Hollert, H., Ros-Nickoll, M., Schäffer, A. and Scheringer, M. (2019): Future pesticide risk assessment: narrowing the gap between intention and reality. - Environ Sci Eur (2019) 31:21

Stähler, M. (1993): Niederschlagsmonitoring im Land Brandenburg. –Nachrichtenbl. Deut. Pflanzenschutzd., 45 (2), S. 32-36 https://ojs.openagrar.de/index.php/NachrichtenblattDPD/article/view/8087